PRESERVATION OF HIDES WITH SULFITE. IV. A STUDY OF METHODS OF APPLICATION

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Abstract

A large-scale test in cooperation with a tannery has shown that a proposed system for short-term preservation of hides that might be used in slaughterhouses instead of salt curing can be adapted commercially to produce acceptable side upper leather. The method preserves hides for about 7 days, and involves treatment with sodium sulfite and acetic acid. A practical limitation of the process used in this test was that the chemicals were applied by drumming. Most slaughterhouses, where an estimated 2 to 5 million hides are taken off each year, are too small to justify investment in commercial drumming equipment.

We have now developed and evaluated four methods of applying the acid-sulfite preservation treatment which require little or no investment in equipment: (1) Sprinkle solid sodium bisulfite on the flesh surface of the hide, fold, containerize, and store; (2) store the hide submerged in the treatment solution in a covered container; (3) apply treatment solids to the hide in a lined 55-gal drum, agitate on a drum roller and store; (4) add treatment solution to the hides in a lined 55-gal drum, agitate on a drum roller and store. In methods 3 and 4 the same container can be used to treat, store, and ship the hides.

Use of these acid-sulfite preservation methods in place of salt curing when hides need to be preserved for only 6 days would significantly lower the dissolved solids and sodium ion content of beamhouse effluents.

Introduction

There is a trend in this country for tanners to make leather from fresh hides when they are available. This trend should be encouraged, since studies have shown that processing fresh hides instead of brine-cured ones conserves water, energy, and capital, and eliminates water pollution by dissolved salt at both the curing and tannery sites (1, 2).

*Agricultural Research Service, U.S. Department of Agriculture.

the experimental treatments is a Morse Model 200 VSM Rotator*. The 55-gal drums used to treat hides on the drum roller and then to hold them in storage, were supplied by Natico, Inc. Each drum had a polyethylene insert and a steel cover protected by a polyethylene disc and gasket. Any simple drum roller should prove adequate and the drums could also be solid polyethylene, fiber glass, or fiber, provided they are strong enough and inert to the treatment ingredients. In small-scale experiments, samples were stored at 30°C and in large-scale experiments the hides were stored at ambient temperatures. When salt-cured hides were used as matched-side controls, the salt curing was done commercially.

ANALYTICAL METHODOLOGY AND PHYSICAL TESTING.

When sides or hides were tested usually three samples, of approximately 50 to 100 g each, were cut from the edges. If possible, one sample was taken from the exposed top surface of the hide, another from the interior of the folds, and a third from the bottom of the hide. Microbial counts were determined by adding 500 ml of sterile water to the sample jars and shaking the jars for 15 min on a reciprocating shaker at approximately 200 rpm. The pH of these bacterial wash solutions was determined and serial dilutions were made from them. Samples from each dilution were plated in duplicate, using standard plate count agar as the media, and the plates were counted after 48- to 72-hr incubation at 30°C. In small-scale studies the whole sample was used to obtain microbial count data.

The preserved hides were processed commercially to leather and given a subjective evaluation by the tanner who processed them. The experimental leathers were tested for tensile strength (10) and SATRA grain crack (11, 12). This latter test was performed according to the methods of the International Union of Leather Technologists' and Chemists' Societies where it is called the "Ball Burst Test."

METHODS OF APPLICATION.

The following four methods of application were studied for treating hides with the acid-sulfite preservative. Caution must be exercised with acid solutions containing the sulfite ion because sulfur dioxide is a toxic gas with an offensive odor.

Method I — Solid $NaHSO_3$. The hides were spread out on a plastic sheet with the flesh surface up. Solid $NaHSO_3$ (2 or 3 percent of the weight of the hide) was sprinkled over the flesh side so as to cover this whole surface uniformly. The hide was folded into a bundle, placed in a polyethylene bag, and sealed. The sealed bags were stored in fiber glass boxes at ambient temperatures. Hide samples were folded and placed in Mason jars, plastic bags, or plastic boxes, and the containers were sealed for storage.

Method II — Sodium Sulfite-Acetic Acid Solution. Hides or samples were immersed in a preservative solution consisting of 1 percent Na_2SO_3, 1 percent acetic

acid, 50 percent water, and 0.03 percent Tergitol 15-S-9. All concentrations were based on the weight of the sample or hide. Hide samples were pushed beneath the surface with a glass rod. The sides were treated by immersing them in the solution in a plastic garbage can lined with a polyethylene bag. They were pushed into the solution with a wooden paddle to get rid of trapped air pockets which buoyed them up. The plastic bag was sealed and the sides were stored in the solution.

Method III — Agitation in Drum with Solid $NaHSO_4$ and $NaHSO_3$. On the flesh side of the hide was added 1.0-to 1.5 percent $NaHSO_4$, the hide was transferred to a container and 1 percent $NaHSO_3$ was added on the upper hair surface of the hide. The $NaHSO_4$ and $NaHSO_3$ were carefully kept apart from each other to prevent or minimize any sulfur dioxide evolution until the container was sealed. Containers for the hide samples were either ½-gal or 1-gal brown, wide-mouthed jars, and for the sides, 55-gal plastic-lined drums. The containers were sealed and placed on a roller. The jars were rolled for 1 hr at 11 or 60 ppm on two different fixed-speed rollers. The 55-gal drums were rolled at 15 rpm for 1.5 hr. The hides or samples were held in storage in these containers.

Method IV — Agitation in Drum with $NaHSO_3$ and Acid Solution. To the flesh (or hair) surface of the hide was added 1 percent $NaHSO_3$. The hide sample was transferred to a container in such a way as to maintain the $NaHSO_3$ in the interior folds of the hide. Thus, when the acid solution was added, immediate contact with the sulfite salt was prevented. In this way, little or no sulfur dioxide gas was generated until the container could be sealed, an important precaution with a strong solution such as sulfuric acid. The acid solution added was 20 percent water, 1 percent NaCl and 1 percent of either acetic or sulfuric acid, all based on the weight of the hide. The samples were treated in brown, wide-mouth jars of ½- to 1-gal capacity. The jars were sealed and rolled on a fixed-speed roller at 11 rpm for 1 hr. A 55-gal drum lined with polyethylene was used to treat the hides and it was rolled at 15 rpm for 1.5 hr. The hides and samples were stored in these containers.

Lime should be used to raise the pH of hides preserved with acid sulfite before they are unhaired; otherwise, sulfhydrate in the unhairing solution could cause toxic hydrogen sulfide to evolve. This is an essential precaution. In addition, tannery-scale tests carried out at Seton Leather indicated that a slightly lighter-than-normal weight of upper leather results if the hides are unhaired in a condition of low pH (13).

Results and Discussion

METHOD I — SOLID $NaHSO_3$.

Hide Samples. Various concentrations of $NaHSO_3$ were sprinkled over the flesh surface of a hide sample as described above. Table I shows that if hide is fleshed and demanured, a concentration of 2 percent $NaHSO_3$ will protect it against microbial attack, and that hides so prepared and treated will keep for 52 days.

One sample appeared good by observation after one year. It had no off-odor or obvious microbial growth, but it was inadvertently discarded without determining the bacterial count.

Where the hide samples were not fleshed or demanured, the microbial numbers were higher, as were the pH's of the bacterial wash solutions. This is probably because the samples initially had relatively higher bacterial numbers and were more alkaline.

TABLE I

PRESERVATION OF HIDE SAMPLES WITH SOLID $NaHSO_3$ (METHOD I)[a]

Condition of hide	$NaHSO_3$ (%)	Storage time (days)	Bact. wash pH	Bact./g hide[b]
	1.0	3	–	bad
	1.5	5	–	bad
	2.0	32	4.4	1,000
Fleshed and demanured				
	2.0	14	–	1,000
	2.0	35	4.3	1,000
	2.0	52	4.6	2,000
	2.0	365	–	good
Not fleshed or demanured	2.0	7	5.2	450,000
	2.0	11	5.0	9,000
	2.0	87	4.3	11,000

[a] $NaHSO_3$ sprinkled on flesh side, samples folded and stored at 30°C.

[b] Where no counts were made, subjective evaluation is indicated, based on visual inspection.

Sides. This method of treatment was tested on full sides using three cowhides that were neither fleshed nor demanured. Each of the hides was cut into matching sides. One was treated by spreading 2 percent $NaHSO_3$ on the flesh surface and the other was commercially cured.

The sides held 7 days had no visible microbial growth, nor did they have any off-odor or odor of sulfur dioxide. However, after 28 days, two of the sides did show a few small spots of growth on the upper exposed hair surface of the folded sides. The remaining areas of the sides appeared satisfactory and no odor of sulfur dioxide was noted.

Table II lists the microbiological data obtained from the experimental and salted sides after 7 and 28 days of storage. The microbial counts and wash pH's of the treated hides are significantly higher than those obtained from small sample studies. This difference is probably accounted for by a number of factors. One is the sampling method for hides which uses only small samples cut from the edges while the whole sample is used in small-scale work. Many of the samples taken from the hide were flank pieces where hide contamination is concentrated. Also, the hides used in this experiment were not fleshed or demanured, as most of the

TABLE II

COMPARATIVE QUALITY OF GARMENT/LIGHT SHOE UPPER LEATHER MADE FROM COWHIDE PRESERVED WITH 2 PERCENT SOLID $NaHSO_3$ (METHOD I) AND FROM COMMERCIALLY SALT-CURED COWHIDE[a]

			Physical test data on leather			
			Tensile data[c]		SATRA grain crack	
Side[b]	Bact. wash pH	Microbial count	Elongation	Tensile strength	Extension	Break load
		bact./g hide × 10^3	percent	psi	mm	kg
			7-day storage			
1A	6.1	2,100	48	2075	9.35	30
B	7.3	10,800	42	2020	9.83	31
2A	6.5	54,000	48	2290	9.78	37
B	7.1	4,900	49	2225	9.83	31
3A	6.2	925	55	2265	9.05	18
B	—	—	54	1900	8.58	16
			28-day storage			
4A	6.2	472	44	2040	9.08	30
B	6.8	316	44	2315	9.28	30
5A	6.3	137	62	1960	9.61	30
B	6.9	495	39	2000	9.65	34
6A	6.3	1,200	36	2095	8.25	24
B	6.8	530	53	2000	11.01	31

[a] Not fleshed or demanured. Stored at ambient temperatures (approx 70°F).

[b] Side A experimental, side B matching commercial salt cure.

[c] Average of three determinations run parallel to the backbone.

small samples were. Another factor is the way treated hides were bundled as compared to the hide samples which were usually only folded over once. This bundling tends to prevent any sodium bisulfite solution formed or any sulfur dioxide evolved from contacting the outer hair surface over which much of the hide's microbial contamination is distributed. However, microbial control is indicated since untreated sides held 7 days under similar conditions would have a putrid odor, grain damage, and bacterial counts in the billions per gram of hide (5).

The sides were taken to a tannery and were processed into upholstery leather. Table II shows that the tensile values and SATRA grain crack extensions of the experimental sides and matched salted control sides were comparable after 7- and 28-day storage periods. A SATRA extension at grain crack of 7.0 mm or higher indicates a leather satisfactory for lasting in most cases; since these values were all above 7.0 mm, the leathers could be expected to have good lasting properties. There was no obvious difference between the crust leathers from the experimental sides of the salted control sides and the leather was judged acceptable by the tanner.

Method II — Sodium Sulfite - Acetic Acid Solution

Hide Samples. Samples of fleshed, demanured steer hides were stored in a sodium sulfite solution as described above and then tested after 10, 16, and 28 days.

The pH's of the bacterial wash were consistently 5.1 and the microbial counts averaged 4,000 bacteria per gram of hide. At this pH, the odor of SO_2 was negligible since the concentration of H_2SO_3 is extremely low (14). Two samples were removed from this solution after 10 days, drained 1 min, and held an additional 6 days. They still gave low bacterial counts averaging 6,000 bacteria per gram of hide and wash pH was 5.1.

Sides. Three cowhides which had not been fleshed and demanured were sided. One side received a commercial salt cure and the other side was added to a 50-percent treatment float. After 6 days the three experimental sides were removed from the solution and sampled for bacterial counts. Table III shows that the counts on the treated sides were much lower than on the salted controls, indicating, in this case, the effectiveness of the treatment in reducing the count.

TABLE III

COMPARATIVE QUALITY OF UPHOLSTERY LEATHER (CRUST) MADE FROM COWHIDE[a] IMMERSED 6 DAYS IN SODIUM SULFITE SOLUTION (METHOD II) AND FROM COMMERCIALLY SALT-CURED COWHIDE

			Physical test data			
			Tensile data[c]		SATRA grain crack	
Side[b]	Bact. wash pH	Microbial count	Elongation	Tensile	Extension	Break load
		bact./g hide	percent	psi	mm	kg
1A	5.1	22,000	47	2010	8.10	23
B	6.5	1,400,000	47	2380	8.65	32
2A	5.0	32,000	40	2350	8.95	29
B	6.5	1,100,000	35	3650	9.05	28
3A	5.1	43,000	51	2545	8.35	25
B	6.9	500,000	72	2135	8.70	23

[a] Not fleshed or demanured. Stored at ambient temperatures (approx 70°F).
[b] Side A experimental, side B matching commercial salt cure.
[c] Average of three determinations run parallel to the backbone.

The sides were processed into upholstery leather to the crust state. Tensile values were comparable between the controls and experimental sides except for control side 2 which had a tensile value much higher than the other controls or the experimental leather. The SATRA extensions were all well above 7.00 mm. The tanner commented that for upholstery use the leather was slightly on the loose side. But he judged the two matched sides in each case to be comparable, so that the looseness was not attributable to the experimental method of hide preservation.

Short-Term Immersion. Additional experiments were done with Method II in which hide samples were removed from the preservative solution after 6 and 24 hr instead of holding them in the solution during storage. After the samples were drained for 15 min, they were sealed in quart Mason jars and stored at 30°C.

The hides were processed into garment/light shoe upper leather to the crust stage. The physical test data showed tensile values averaging 1660 psi and the SATRA extensions were all greater than 7.00 mm. The tanner's judgment was that the leather quality was very good.

METHOD IV — AGITATION IN DRUM WITH $NaHSO_3$ AND ACID SOLUTION

Hide Samples. This method, in which sodium bisulfite is added in the float with an acidulant and the hide is agitated on a roller, was first tested on hide samples and the results are summarized in Table VII. Acetic and sulfuric acids were tested as the acidulants on samples of fleshed and demanured cow- and steerhide. Microbial control was maintained for at least 36 days when sulfuric acid was used with bisulfite.

TABLE VII

PRESERVATION OF HIDE SAMPLES[a] BY AGITATION[b] IN SOLUTION OF SODIUM BISULFITE AND TWO DIFFERENT ACIDULANTS (METHOD IV)

Sample	Acidulant		$NaHSO_3$	Storage time	pH of bact. wash	Bacteria/ g of hide
	Acid	Conc.				
		%	%	days		
1	HAc	0.5	1.0	13	4.5	26,000
2	HAc	1.0	0.5	13	4.3	6,000
3	HAc	1.0	1.0	14	—	9,000
4	H_2SO_4	0.5	1.0	8	4.6	6,000
5	H_2SO_4	0.5	1.0	15	4.7	2,000
6	H_2SO_4	0.5	1.0	36	4.6	4,000

[a] All fleshed and demanured except No. 3.

[b] Rolled for 1 hr at 11 rpm.

TABLE VIII

QUALITY OF GARMENT/LIGHT SHOE UPPER LEATHER MADE FROM COWHIDE[a] PRESERVED WITH SODIUM BISULFITE AND ACETIC ACID (METHOD IV) AND STORED 6 DAYS

Side[d]	Bact. wash pH	Microbial count	Physical test data on leather			
			Tensile data[c]		SATRA grain crack	
			Elongation	Tensile strength	Extension	Break load
		bact./g hide	percent	psi	mm	kg
1R	4.4	6,000	49	2435	10.00	34
1L			45	1975	9.35	34
2R	4.3	3,000	51	2305	9.05	17
2L			33	1430	7.20	14
3R	4.3	8,000	36	1465	7.40	12

[a] Not fleshed or demanured, held at ambient temperature (approx. 70°F).

[b] Rolled for 1.5 hr at 15 rpm.

[c] Average of three values, run parallel to backbone.

[d] R = right; L = left; left side of No. 3 lost in process.

Sides. Three cowhides, not fleshed or demanured, were treated as explained earlier, and were held in the treatment drum for 6 days. Table VIII shows that microbial control was maintained for this period of time. These hides were sided and then processed into garment/light shoe upper leather to the crust stage. The first three (sides 1R, 1L, and 2R) were processed into heavier leathers than the others, accounting for the variation in the physical test data. This is most apparent within the matching sides 2R and 2L. Side 3L was lost. In the judgment of the tanner, the leathers produced were comparable to normal production.

In Methods III and IV the treatment involves either the use of solid salts or a 20 percent float containing the sulfite salt and acid. Work at our laboratory has shown that gaseous sulfur dioxide alone can be used to preserve hides for at least 28 days (15 - 17). The gas, either alone or as a sulfurous acid solution, could probably be used in the above methods. A particular advantage in its use is the relatively low cost of sulfur dioxide.

Treatment and Storage Containers for Hide Preservation

Protecting a hide from further contamination or loss of preservative ingredients is an important aspect of any preservation. Using the same container to treat, store, and ship a hide meets this requirement and eliminates the need for handling or exposing the hide until it needs to be processed. Further work is needed however to determine the best drum design and agitation methods as well as to gain more experience data with this process. Fiber glass, high-density polyethylene or fiber drums could be used if they are strong enough and if they are inert to the corrosive effects of the treatment ingredients. The drums should also be reusable. A drum tumbler, for example, in which the drum is rotated around its horizontal axis might give a more vigorous agitation to the hides than a drum roller. Rectangular containers could be adapted for use with the drum ruller or tumbler if desired. But the fact that drums can be rolled makes them especially adaptable to loading and unloading.

Summary and Conclusions

Four application methods were evaluated for the acid-sulfite treatment developed at this laboratory for hide preservation. They all gave satisfactory protection against microbial attack for at least 6 days, and the treated hides were commercially processed into acceptable leather.

Method I. The use of solid $NaHSO_3$ (2 and 3 percent on the weight of the hide) spread uniformly over the flesh surface of the hide demonstrated that short-term preservation could be accomplished by treating just the flesh surface of the hide. This surface is relatively uncontaminated when a hide is removed from an animal, and a treatment applied to it at this time could provide short-term preservation by (1) protecting this surface from further contamination and (2) penetrating the flesh side to inhibit or inactivate enzymes and bacteria. This assumes that the

grain surface will provide a temporary barrier to the heavy microbial contamination present on this surface.

Method II. Immersing the hides in a 50 percent float of 1 percent acetic acid and 1 percent Na_2SO_3 during storage also appears to be a promising approach. On a small scale, samples held in these solutions for 6 to 24 hr and then drained of excess solution have maintained microbial control for approximately 2 weeks at 30°C. This indicates that hides can be held in treatment solutions for 6 to 24 hr or until ready to be shipped. At this time the hides can be drained of excess solution and packaged with the potential of maintaining microbial control for at least 2 to 3 days for shipment to a tannery.

Methods III and IV. The use of a lined 55-gal drum agitated by a drum roller demonstrates a simple and effective way to apply a preservation treatment. It can be used to control the sulfur dioxide odor associated with the acid sulfite treatment. The use of an appropriately designed drum to treat, store, and ship preserved hides is a novel and yet practical concept that could prove to be useful in both small and large operations. The preserved hide would be protected from further contamination, damage, or loss of treatment chemicals until the drum was opened for use. This could act to prolong the preservation time.

If the same container is used to treat, store, and ship the hides, any sulfur dioxide odor can be eliminated by introducing an alkaline solution into the drum before opening. Raising the pH of this system to 6.0 or higher will cause any sulfur dioxide odor to disappear. The hides are then ready to be sorted, washed, or processed.

We feel that this work has satisfied our objective of demonstrating that acid sulfite can be applied to hides for short-term preservation by methods that require little or no capital investment in equipment. They vary in chemical costs, equipment requirements, and final shipping weights, providing a choice based on local needs. The use of an appropriate 55-gal drum for treatment, storage, and shipment is a way of overcoming the sulfur dioxide odor problem which is critical to the adoption and use of the acid-sulfite preservation. Some of the methods and concepts described in this study could be applied to other preservation systems. Additional work is needed to gather more extensive experience data under planned use conditions and to design and test appropriate containers that can be reused.

Acknowledgment

The author thanks the following people for their cooperation: Dr. Stephen Feairheller and Mr. Joe Cheskiewicz of our laboratory, and Mr. Satyendra De of Garden State Tanning, and Messrs. Jim Jennings, Ben Kulik, and Dave Small of H. Swoboda & Sons.

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